Ideal and Non-Ideal solution

(1) **Ideal solution :** An ideal solution may be defined as the solution which obeys Raoult's law over the entire range of concentration and temperature and during the formation of which no change in enthalpy and no change in volume takes place. So for ideal solutions the conditions are,

(i) It should obey Raoult's law, *i.e.*, $P_A = P_A^0 X_A$ and $P_B = P_B^0 X_B$.

(ii) $\Delta H_{mixing} = 0$

(iii) $\Delta V_{mixing} = 0$

The solutions in which solvent-solvent and solute-solute interactions are almost of the same type as solvent-solute interactions, behave nearly as ideal solutions.

This type of solutions are possible if molecules of solute and solvent are almost of same size and have identical polarity. For example, solutions of following pairs almost behave as ideal solutions,

n-Heptane and *n*-hexane.; Chlorobenzene and bromobenzene.

Benzene and toluene; Ethyl bromide and ethyl iodide.

Ethylene bromide and ethylene chloride; Carbon tetrachloride and silicon tetrachloride.

For such solutions the vapour pressure of the solution is always intermediate between the vapour pressures of pure components *A* and *B*, *i.e.*, P_A^0 and P_B^0.

(2) **Non-Ideal solution :** The solutions which do not obey Raoult's law and are accompanied by change in enthalpy and change in volume during their formation are called non-ideal solutions. so, for non-ideal solutions the conditions are :

(i) It does not obey Raoult's law. $P_A \neq P_A^0 X_A$; $P_B \neq P_B^0 X_B$

(ii) $\Delta H_{mixing} \neq 0$

(iii) $\Delta V_{mixing} \neq 0$

Either component of non-ideal binary solution do not follow Raoult's law. The non-ideal solutions are further divided into two types :

(a) Solutions showing positive deviations

(b) Solutions showing negative deviations

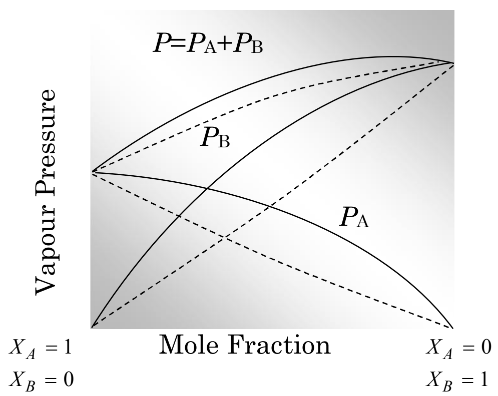
(a) **Solutions showing positive deviation :** In this type of deviations, the partial vapour pressure of each component (say A and B) of solution is greater than the vapour pressure as expected according to Raoult's law. This type of deviations are shown by the solutions in which solvent-solvent and solute-solute interactions are stronger than solvent-solute interactions.

For the non-ideal solutions exhibiting positive deviation.

$P_A > P_A^0 X_A$, $P_B > P_B^0 X_B$; $\Delta H_{mixing} = +$ ve;

$\Delta V_{mixing} = +$ ve

e.g. of solutions showing positive deviations



Partial and total vapour pressure curves for solutions that show positive deviations from Raoult's law

$(CH_3)_2CO + CS_2$; $(CH_3)_2CO + C_2H_5OH$

$C_6H_6 + (CH_3)_2CO$; $CCl_4 + C_6H_6$

$CCl_4 + CHCl_3$; $CCl_4 + C_6H_5CH_3$

$H_2O + CH_3OH$; $H_2O + C_2H_5OH$

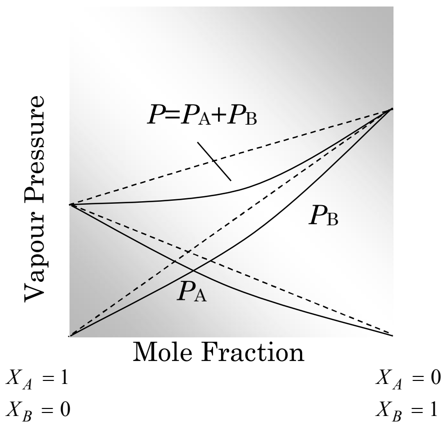
$CH_3CHO + CS_2$; $CHCl_3 + C_2H_5OH$

(b) **Solutions showing negative deviation :** In this type of deviations the partial vapour pressure of each component of solution is less than the vapour pressure as expected according to Raoult's law. This type of deviations are shown by the solutions in which solvent-solvent and solute-solute interactions are weaker than solvent-solute interactions.

For non-ideal solution showing negative deviation.

$P_A < P_A^0 X_A$, $P_B < P_B^0 X_B$; $\Delta H_{mixing} = -$ ve;

$\Delta V_{mixing} = -ve$



A vapour pressure curve showing negative deviation (solid lines) from ideal behaviour (dotted lines)

e.g. of solutions showing negative deviations

$CH_3COOH + C_5H_5N$ (pyridine)

$CHCl_3 + (CH_3)_2CO$; $CHCl_3 + C_6H_6$

$CHCl_3 + (C_2H_5)_2O$; $H_2O + HCl$

$H_2O + HNO_3$; $(CH_3)_2CO + C_6H_5NH_2$

Differences between ideal and non-ideal solutions

Ideal solutions	Solutions with positive deviations	Solutions with negative deviations
$A......B$ interactions are similar to $A......A$ and $B......B$ interactions	$A......B$ interactions are smaller than $A......A$ and $B......B$ interactions	$A......B$ interactions are greater than $A......A$ and $B......B$ interactions
$P_A = P_A^0 X_A;\ P_B = P_B^0 X_B$	$P_A > P_A^0 X_A;\ P_B > P_B^0 X_B$	$P_A < P_A^0 X_A;\ P_B < P_B^0 X_B$
$\Delta H_{sol.} = 0$	$\Delta H_{sol.} > 0$	$\Delta H_{sol.} < 0$
$\Delta V_{mix} = 0$	$\Delta V_{mix} > 0$	$\Delta V_{mix} < 0$
Do not form azeotrope	form minimum boiling point azeotrope	form maximum boiling azeotrope

Azeotropic mixture

Azeotropes are defined as the mixtures of liquids which boil at constant temperature like a pure liquid and possess same composition of components in liquid as well as in vapour phase. Azeotropes are also called constant boiling mixtures because whole of the azeotropes changes into vapour state at constant temperature and their components can not be separated by fractional distillation. Azeotropes are of two types as described below :

(1) **Minimum boiling azeotrope :** For the solutions with positive deviation there is an intermediate composition for which the vapour pressure of the solution is maximum and hence, boiling point is minimum. At this composition the solution distills at constant temperature without change in composition. This type of solutions are called minimum boiling azeotrope. *e.g;*

Components		Mass % of *B*	Boiling points (*K*)		
A	**B**		**A**	**B**	Azeotrope
H_2O	C_2H_5OH	95.57	373	351.3	351.1
H_2O	$C_2H_5CH_2$C	71.69	373	370	350.72
$CHCl_3$	C_2H_5OH	67	334	351.3	332.3
$(CH_3)_2$C	CS_2	6.8	329.25	320	312.2

(2) **Maximum boiling azeotrope :** For the solutions with negative deviations there is an intermediate composition for which the vapour pressure of the solution is minimum and hence, boiling point is maximum. At this composition the solution distill`s at constant temperature without the change in composition. This type of solutions are called maximum boiling azeotrope. *e.g*

Components		Mass % of *B*	Boiling points (*K*)		
A	**B**		**A**	**B**	Azeotrope
H_2O	HCl	20.3	373	188	383
H_2O	HNO_3	58.0	373	359	393.5
H_2O	$HClO_4$	71.6	373	383	476